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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Mixtures of Liquids or Pastes with Finely Divided Orthophosphates

We, CHEMISCHE FABRIK KALK G.M.B.H. Koln-Kalk, Kalker Hauptstrasse 22, Federal Republic of Germany, a body corporate organised under the Laws of Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to mixtures of liquids or of pastes with finely divided phosphates to which they are chemically inert.

As is known, liquids or pastes can be thickened to the point of solidification by mixing with finely divided oxides of metals or metalloids. Particularly suitable for this purpose is a highly dispersed silicon dioxide, having a particle size between 0.004 and 0.02μ and a specific surface of 174 to 400 m^2/g. It is added to the liquids or to the pastes in quantities from 1 to 20% by weight. This highly dispersed silicon dioxide, however, has the disadvantage that it readily forms lumps on being incorporated by stirring into liquids and these lumps are only removed by further stirring with very great difficulty. In addition, this highly dispersed silicon dioxide is hydrated very quickly, in water-containing liquids or pastes. On account of these properties, the highly dispersed silicon dioxide is not suitable without preliminary treatment, for example, for thickening aqueous synthetic plastic dispersions, since it extracts so much water by hydration from the dispersions that the dispersed phase coagulates.

Accordingly, an attempt has been made to find other finely divided substances which can be used without the aforementioned disadvantages as a thickening agent for liquids or pastes.

Mixtures of liquids or pastes with finely divided phosphates have now been discovered which do not present these disadvantages. These mixtures consist of 1 to 50% by weight, advantageously 3 to 10% by weight, of finely divided phosphates which are chemically inert to the liquids or pastes and which are sparingly soluble in water and are present substantially in the ortho-form, which phosphates have average particle size below 0.03μ advantageously from 0.005 to 0.02μ. For simplifying the description, these phosphates are hereinafter referred to as "finely divided phosphates."

In the finely divided phosphates, divalent metals or aluminium or mixtures thereof should be present as cationic constituents in such quantities that the $MeO:P_2O_5$ or the $Me_2O_3:P_2O_5$ molar ratio in the finely divided phosphates is 0.5:1 to 3.5:1, where Me represents the cationic constituent. In order to obtain the finely divided phosphates it is preferred initially to mix together orthophosphoric acid and salts which contain divalent metals or aluminium or mixtures thereof as cation and the anionic radical of a strong readily volatile acid, such as nitric acid, hydrochloric acid, as anion in suitable proportions to form a clear solution or a paste. These mixtures are then sprayed into a hot stream of an inert gas such as air or combustion gases, which is at temperatures of 190 to 450°C. The finely divided phosphates which are formed as end product are substantially in ortho-form and their bulk density is between 5 and 350 g/l, advantageously between 8 and 80 g/l. Their average particle size is below 0.03μ. The particles of these finely divided phosphates can also be agglomerated to form loose and porous compounds. The development and the form of these agglomerates depend essentially on the chemical composition of the

[*Price 4s. 6d.*]

ERRATA

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Page 1, line 49, *for* "size" *read* "sizes"
Page 3, line 19, *for* "or" *read* "of"
Page 5, Table 1, 7th column, *for* "90.1" *read* "0.1"

THE PATENT OFFICE
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corresponding finely divided phosphates and also on the starting materials used for the production thereof and the conditions which are maintained during production. Thus, the particles with a size of about 0.01μ and consisting of tricalcium phosphate produced from orthophosphoric acid and calcium nitrate form loose, porous round agglomerates with a diameter of 0.05 to 3.0μ diameter or elongated agglomerates with a length of about 3.0μ, which are constructed in a manner similar to a string of pearls. In products formed by spraying calcium chloride and orthophosphoric acid, the primary particles with a size of about 0.01μ agglomerate as porous rods or cords with a length of 1 to 5μ.

One may also employ finely divided phosphates which have been produced by other processes as constituents of the mixture. The most desirable thickening action for liquids or pastes is only obtained, however, if these finely divided phosphates have an average particle size below 0.03μ and bulk densities from 5 to 350 g/l, advantageously 8 to 80 g/l.

Before being mixed with the liquids or the pastes, the finely divided phosphates can also be mixed with other finely divided substances, of which the particles are larger in size than those of the finely divided phosphates. For the production of such mixtures, it is of course only possible to employ substances which do not react chemically with the finely divided phosphates. Such mixtures have the same thickening action on liquids or on pastes as the finely divided phosphate itself, which is contained in these mixtures.

As the second component, the mixtures according to the invention contain liquids, as for example pure substances which are liquid at normal temperature, or mixtures thereof, such as contain oils, solutions, dispersions, or emulsions, or pastes for example certain paraffins, fats, waxes, bitumen, tar, and asphalt. These liquids or pastes should not react chemically with the finely divided phosphates.

The viscosity of liquids can be increased until solid masses are formed if the finely divided phosphates are slowly incorporated by stirring into the liquids. Since the finely divided phosphates have a substantially lower affinity for water than for example highly dispersed silicon dioxide, the finely divided phosphates can in this way be mixed without lump formation with water or liquids which contain water. Thus, gel-like mixtures are for example formed if 5 to 20% by weight of a finely divided phosphate is slowly incorporated by stirring into aqueous solutions or suspensions of inorganic substances, such as for example potassium carbonate solution or calcium hydroxide suspensions. In this manner also, electrolyte solutions can also be thickened by adding 15% by weight of a finely divided zinc phosphate so that they can be used as an electrolyte composition in pocket lamp batteries. It is also possible for organic liquids, as for example benzene, chlorobenzene, *p*-dichlorobenzene, toluene and formaldehyde to be solidified into stiff pastes by incorporating slowly by stirring 1 to 10% by weight of a finely divided phosphate. Aqueous sodium silicate solutions (water glass) solidify immediately into a hard solid mass after adding 6% by weight of a finely divided phosphate. Aqueous dispersions and emulsions, such as for example synthetic resin dispersions, can be solidified by slowly stirring in about 5% by weight of a finely divided phosphate without the dispersed or emulsified phase coagulating. Furthermore, solid, gel-like pastes can be produced from oils by slowly stirring in about 10 to 20% by weight of finely divided phosphates. Soap solutions which *per se* tend to become string-forming after standing for a short time can be transformed into a non-stringing paste by slowly stirring in about 17% by weight of a finely divided phosphate, which paste can be pressed into tablets.

The addition of smaller quantities of finely divided phosphates causes at least a thickening of the liquid concerned. Thus, lacquers and paints which contain a quantity of finely divided phosphates insufficient for gelation can for example be brushed on without string formation and without dripping, Because of their fine particle size the finely divided phosphates are also excellent delustering agents for lacquers and paints. The finely divided phosphates which are sparingly soluble in water generally act as dispersion auxiliaries. They prevent a sedimentation of the dispersed phase and with dispersed substances of particularly high specific gravity, facilitate a redispersion of the sediment by stirring. Small quantities of a finely divided phosphate reduce the tendency of adhesives to form filaments and increase the setting strength thereof.

The finely divided phosphates, more especially finely divided calcium ortho phosphates, can be used with particular advantage as thickening agents and dispersion auxiliaries in foods cosmetic or pharmaceutical preparations, such as for example liquids, ointments, pastes or jellies. As compared with other fillers, such as highly dispersed silicon dioxide, the finely divided calcium phosphates have the advantage that they contain elements, namely calcium and phosphorus which are necessary for the nourishment of the human or animal body. The extraordinary fine particle size of these phosphates facilitates their capacity for being absorbed by the human or animal body. The fineness of the finely divided calcium ortho phosphates which are incorporated for thickening purposes into toothpaste also produces a good polishing effect.

The finely divided phosphates may be incorporated by kneading at normal temperatures into pastes for example, certain paraffins, fats and waxes, and tar, and bitumen. The phos-

phates may also be incorporated by heating these substances above their softening point and incorporating the phosphates therein slowly by stirring. The finely divided phosphates produce an increase in the softening points of these substances.

Before being mixed with liquids or pastes the finely divided phosphates can also be impregnated with active substances of all types, such as for example insecticides, and fungicides. For this purpose, the finely divided phosphates are initially impregnated with a suspension or solution of these active substances and the suspension medium or solvent is evaporated from these mixtures. Readily volatile liquids are advantageously used in the active substance suspension or solution. It is also possible for the active substances to be sprayed in the form or liquids, as for example solutions and melts onto the finely divided phosphates.

Dimensionally stable products are obtained if the liquids or pastes are sprayed onto the finely divided phosphates, advantageously by fluidising the latter in a fluidising chamber and spraying the liquid or the paste on the fluidised particles in the said chamber. By this means, it is possible to produce solid mixtures which are capable of trickling and which contain up to 70% by weight of liquid. Despite their high liquid content, these mixtures can be stored for a practically unlimited period without the individual particles sticking or caking together. Generally speaking, the finely divided phosphates treated in this manner can still be wetted satisfactorily with water, even when the added substances are water repellant.

The mixtures according to the invention have the advantage that they can be produced more simply than the mixtures which contain the highly dispersed silicon dioxide which readily forms lumps during processing, since the finely divided phosphates do not show any tendency to lump formation, even in the presence of liquids. In addition the finely divided phosphates are hydrated considerably more slowly than the highly dispersed silicon dioxide formerly used for thickening liquids. The thickening effect of the finely divided phosphates contained in the mixtures according to the invention depends only to an insignificant extent on temperature.

In order that the invention may be more fully understood the following Examples are given by way of illustration only:

EXAMPLE 1.

In order to raise the softening point, there were added to the substance indicated in the Table increasing quantities of a finely divided calcium orthophosphate, the $CaO:P_2O_5$ molar ratio of which was 0.5:1. In order to prepare the calcium orthophosphate, an aqueous solution containing orthophosphoric acid and calcium nitrate in suitable molar proportions was sprayed into an air stream heated to 380°. The particles of the calcium orthophosphate produced in this way had a diameter of about 0.01μ. They had agglomerated to form loose porous balls with a diameter of about 0.1μ. The bulk density of this product was 8 g/l.

	Quantity of phosphate % by weight	Softening Point °C.
Engine oil—SAE Viscosity, Number 30	5 7.5 10	81.5 91 >160
Diesel oil — mixture of paraffins, olefines, naphthenes and aromatic compounds — obtained by distillation from petroleum at 200—300° C. Has specific gravity of about 0.86	3	>160
Stauffer grease — calcium stearate containing a lubricating agent, the drop point of which must be at least 75° C.	0 10 20 30	81 85.5 96 117
Paraffin I. — mixture of saturated aliphatic hydrocarbons with melting point 42—44° C.	0 3 5	42 112 160
Paraffin II — mixture of saturated aliphatic hydrocarbons with a melting point 55—60° C.	0 3 5	55 122 >160
Paraffin III — mixture of saturated aliphatic hydrocarbons with a melting point 63—72° C.	0 2 3	63 90 >160
Carnauba wax	0 5 10	82 87 >160
Tar	0 2 3	104 126 >160

EXAMPLE 2.

5 parts by weight of the finely divided phosphate used in Example 1 were slowly incorporated by stirring into 50 parts by weight of formaldehyde and a pasty mixture having a gel - like character was formed.

EXAMPLE 3.

6 parts by weight of the finely divided phosphate used in Example 1 were incorporated by stirring into 100 parts by weight of glycerine and a thixotropic paste was formed.

EXAMPLE 4.

3.5 parts by weight of a finely divided phosphate were slowly incorporated by stirring into 87 parts by weight of benzene. The finely divided phosphate was produced in accordance with the details given in Example 1, by spraying an aqueous solution which contained calcium chloride and ortho phosphoric acid in a molar ratio 3.3 : 1 into an air stream at 380°C. The particles of this finely divided phosphate had a diameter of 0.01μ. These particles agglomerated to form small porous rods with a length of about 0.1μ and a diameter of 0.01 to 0.15μ. The mixture is a thixotropic paste.

EXAMPLE 5.

In order to determine the dependence on temperature of the thickening action of the finely divided phosphates, the experiments described below were carried out.

The finely divided phosphates used in these experiments were prepared under the conditions indicated in Example 1 from aqueous solutions of ortho phosphoric acid and calcium chloride or calcium nitrate. The composition of the spraying solution and the characteristic features of the sprayed products are apparent from the following Table I.

TABLE 1

Designation of phosphate	Ca-compound used in Initial Solution	Molar ratio CaO/P_2O_5 in End Product	Diameter of particles in μ of End Product	Form of agglomerates	Length of agglomerates in μ	Diameter of agglomerates in μ
A	$Ca(NO_3)_2$	0.5:1	0.01	small balls	—	90.1
B	$Ca(NO_3)_2$	3:1	0.01—0.02	strings of pearls	3	0.01—0.02
C	$Ca(NO_3)_2$	3.3:1	0.01—0.02	small balls	—	0.06—0.1
D	$CaCl_2$	3:1	0.01	small rods	5	0.01—0.2
E	$CaCl_2$	3.3:1	0.01	small rods	1	0.02—0.03

Table II sets out the quantities of the various phosphates referred to in Table I, which quantities have to be added to 100 ml. of the solvents indicated in Table II in order to obtain mixtures of equal consistency at the indicated temperatures.

TABLE II

Solvent	Temperature °C.	Quantity of phosphate in g/100 ml of solvent				
		Phosphate A	Phosphate B	Phosphate C	Phosphate D	Phosphate E
Benzene	20	1.9	3.7	12.5	3.5	3.5
	70	2.0	3.9	11.6	3.5	3.6
Toluene	20	2.8	3.8	11.6	3.5	3.9
	70	2.6	3.8	11.8	3.4	3.6
Chlorobenzene	20	2.4	4.4	11.6	3.7	3.9
	70	2.2	4.5	11.2	3.7	3.6

The results of these experiments show that the thickening effect of the finely divided phosphates is practically independent of the temperature.

EXAMPLE 6.

A solution of 3 g. of aniseed extracts in 100 ml of ether was added dropwise with slow stirring to 47 g. of a finely divided phosphate prepared in accordance with the details given in Example 1. The ether is removed from the mixture by heating for a brief period. A dry product with good trickling properties and capable of being satisfactorily proportioned was formed the product having a bulk density of 22 g/l.

EXAMPLE 7.

315 parts by weight the dinonyl ester of phthalic acid were sprayed onto 250 parts by weight of a finely divided phosphate prepared in accordance with the data of Example 1 and with thorough mixing. A freely trickling powder was formed which had a bulk weight of 350 g/l.

EXAMPLE 8.

To a white-pigmented, air-drying lacquer were added a finely divided phosphate prepared in accordance with the details of Example 1 in the quantities indicated in the following table. The delustering effect of the various additions is also indicated in the Table:

Content of finely divided phosphate in % in lacquer	Lacquer gloss in %
0	100
1	13
2	13
3	4

EXAMPLE 9.

8 parts by weight of a finely divided phosphate prepared according to the data of Example 1 were slowly incorporated by stirring into 92 parts by weight of a mixture which contained 20 parts by weight of ammonium chloride, 10 parts by weight of zinc chloride and 62 parts by weight of water. A paste was formed which could be used as an electrolyte filling for pocket lamp batteries. Even after being stored for several months, this paste did not show any tendency to crystallise.

WHAT WE CLAIM IS:—

1. Mixtures of liquids or pastes with 1 to 50% by weight of the mixture of finely divided phosphates to which they are chemically inert which are sparingly soluble in water and which exist substantially in the ortho-form, the said phosphates having an average particle size of below 0.03μ.

2. Mixtures as claimed in claim 1 in which the finely divided phosphates comprise 3 to 10% by weight of the mixtures.

3. Mixtures as claimed in claim 1 or claim

2 in which the average particle size of the phosphates is from 0.005 to 0.02μ.

4. Mixtures as claimed in any of claims 1 to 3 containing finely divided substances in addition to the finely divided phosphates, the particles of which are larger in size than those of the finely divided phosphates, said other finely divided substances being inert to the other components of the mixture.

5. Mixtures as claimed in any of claims 1 to 4 in which the finely divided phosphates which are sparingly soluble in water have bulk densities from 5 to 350 g/l.

6. Mixtures as claimed in claim 5 in which the bulk densities of the phosphates are from 8 to 80 g/l.

7. Mixtures as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

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